

THERMOANALYTICAL CHARACTERIZATION (DTA AND TGA)

OF

$\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ (R = Y, Gd, Nd) SUPERCONDUCTORS

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ABSTRACT

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) have been used to characterize $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ ($\text{R} = \text{Y}, \text{Gd}, \text{Nd}$) superconductors. Even if the resistivity temperature curves are similar for the three compounds, DTA shows that the behavior of these materials during synthesis and sintering is different. Among the three systems, the Nd-Ba-Cu-O system is the most favorable to the formation of the 123 superconductor because secondary phases are present in smaller quantities. TG curves suggest the presence of a transition from the orthorhombic phase to the tetragonal phase in nitrogen atmosphere at about 550-600°C for the three perovskites. It was also found that the energy required to insert oxygen atoms in the crystal structure is smaller for Nd and Gd compounds than for Y compound ($\text{Gd} < \text{Nd} < \text{Y}$). There is also a proportional relation between the ionic radius of the rare earth element and the onset melting temperature.

INTRODUCTION

According to synthesis conditions and stoichiometries, it is well known that the system Y-Ba-Cu-O can have superconductive properties. The $Y_1Ba_2Cu_3O_{7-x}$ compound has a crystal structure which can be superconducting (orthorhombic) or non-superconducting (tetragonal) depending of the oxygen stoichiometry. A sharp superconducting transition, characterized by an abrupt decrease in resistivity, is observed at about 90 K. Although yttrium has been widely adopted for the making of superconductors, different rare earths were substituted to yttrium in order to verify if they have an effect on the superconducting temperature. Unfortunately, the superconducting temperature is nearly insensitive to the nature of the rare earth element [1-3]. However, the replacement of Y by other rare earths may cause a variation in the reactivity of these perovskites.

In this work, various cuprate perovskites with composition $R_1Ba_2Cu_3O_{7-x}$ ($R = Y, Gd, Nd$) were prepared and characterized using differential thermal analysis (DTA) and thermogravimetric analysis (TGA). It has been shown that the behavior of these materials during synthesis and sintering is different [3], and thermoanalytical characterization can reveal the presence of impurities or secondary phases in $R_1Ba_2Cu_3O_{7-x}$ compounds to explain these variations.

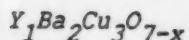
EXPERIMENTAL

Compounds $R_1Ba_2Cu_3O_{7-x}$ ($R = Y, Gd, Nd$) were prepared following a standard ceramic technique. Appropriate amounts of CuO, BaCO₃, Y₂O₃, Gd₂O₃ and Nd₂O₃, each of 99.999% purity, were mixed and calcinated at

950°C for 12 hours in alumina crucibles. The resulting compacts were crushed and sieved to pass through a 400 mesh screen. The heating and crushing steps were repeated a second time, and pellets were pressed from these powders at a pressure of 390 MPa. Pellets were thereafter sintered at 950°C for 6 hours, cooled to 500°C in 1 hour, held at this temperature for 2 hours, and finally cooled to room temperature in about 2 hours. All the thermal treatments were made under a flowing oxygen atmosphere.

The thermal analyzer (DTA and TGA) used was a Model B70 from Setaram (Caluire, France) equipped with a carbon resistance furnace. Data were collected via a Hewlett-Packard system. The balance is accurate to $\pm 30 \mu\text{g}$ over a long period of time. The loss of weight is measured within 0.3%. Samples were analyzed in alumina crucibles. The heating rate was maintained constant at 10 °C/min.

RESULTS AND DISCUSSION



The yttrium perovskite was analyzed in an oxygen atmosphere using DTA and the thermogram is shown in Figure 1. There are three large endothermic peaks at 945°C, 970°C and 1030°C. There are also three small endothermic deflections at about 550°C, 750°C and 810°C.

Gabelica et al [4] also observed three endothermic peaks at 945°C, 980°C and 1032°C associated with a loss of weight but without a definitive identification. Clearly at 1030°C, $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ begins to melt [5,6]. The endothermic peak at 1030°C is associated with the

decomposition of $Y_1Ba_2Cu_3O_{7-x}$ into Y_2BaCuO_5 , $BaCuO_2$ and a liquid [7,8]. The presence of multiple peaks in the DTA curve is probably related to impurities. Using X-ray diffraction, impurities such as $BaCuO_2$ and CuO were detected in pellets made from the $Y_1Ba_2Cu_3O_{7-x}$ powder used in this study [3]. At $810^\circ C$, the small endothermic peak is caused by α - β transition of $BaCO_3$ [5,9]. DTA peaks at $945^\circ C$ and $970^\circ C$ are also probably related to reactions involving carbonates. In air, a similar reaction peak (not identified) at about $940^\circ C$ was observed in an impure material [5]. It was also reported the presence of an endothermic peak at $957^\circ C$ in oxygen atmosphere with the yttrium compound and it was suggested that it could be associated with the formation of an eutectic of the ternary $Y_{0.15}$ - BaO - CuO system.

Figure 1 shows also the DTA of $Y_1Ba_2Cu_3O_{7-x}$ compound obtained with nitrogen atmosphere. There is displacement toward lower temperatures of the main peaks observed in oxygen. The largest endothermic effect occurs at $965^\circ C$ and correspond to the melting of the compound [6]. Clearly, DTA shows the presence of secondary phases which are dependent on the synthesis conditions. Due to the complexity of the chemical reactions involved in these cuprate perovskites, more work will be necessary to identify all these secondary phases.

Figure 2 shows a thermogravimetric curve of $Y_1Ba_2Cu_3O_{7-x}$ obtained in nitrogen atmosphere on heating. There is a significant loss of weight starting at about $440^\circ C$. There is also a small change of slope detected at about $600^\circ C$ followed by a more important loss of weight at $830^\circ C$. The overall weight decrease is attributed to an oxygen loss. The change in the slope at $600^\circ C$ corresponds to the orthorhombic - tetragonal transition. The transition temperature depends on the oxygen

partial pressure and occurs when the stoichiometry is near $Y_1Ba_2Cu_3O_{6.5}$ [6,10,11]. Transition temperatures of 700-750°C [7] and 850°C [4,12] were reported in air and oxygen respectively. However, in oxygen, no loss of weight was observed at the orthorhombic - tetragonal transition [4]. In our case, there is an important loss of weight at 830°C which is probably due to a decomposition of the sample.

Figure 3 illustrates the TG curve on heating of $Y_1Ba_2Cu_3O_{7-x}$ in oxygen atmosphere. There is a gain in weight beginning at 325°C with a maximum at about 490°C (about 1.2%). Thus, the difference between the beginning of the gain in weight and the maximum corresponds to a ΔT of 165°C. From 500°C to 800°C, there is a gradual decrease in weight.

$Gd_1Ba_2Cu_3O_{7-x}$

The crystal structure of $Y_1Ba_2Cu_3O_{7-x}$ is slightly modified when yttrium is substituted by gadolinium [13,14]. Basically, both compounds have a distorted, oxygen-deficient, perovskite structure. Thus, this substitution has almost no effect on the superconducting transition temperature [1-3]. However, the DTA curve of $Gd_1Ba_2Cu_3O_{7-x}$ in oxygen atmosphere, shown in Figure 4, is different of the thermogram of the yttrium perovskite. Many endothermic peaks are detected with onset temperatures of 818°C, 980°C, 998°C, 1038°C, 1050°C, 1055°C and 1075°C. The presence of these peaks indicates that $Gd_1Ba_2Cu_3O_{7-x}$ is impure and contains many secondary phases. As for $Y_1Ba_2Cu_3O_{7-x}$, the peak at 818°C corresponds probably to the α - β transition of $BaCO_3$. At 980°C, there is probably another transformation of $BaCO_3$ to cubic α -form [9]. The presence of $BaCO_3$ has been confirmed using Fourier transform infrared spectroscopy.

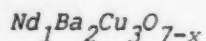
The peak at 998°C is assumed to be due the presence of BaCuO_2 [7,8]. In fact, X-ray diffraction has shown that a significant amount of this product is present in $\text{Gd}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ [3]. With a sintering temperature of 950°C, the replacement of Y by Gd modifies the equilibrium conditions, and then the stability of the superconductor. The melting of $\text{Gd}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ in oxygen atmosphere begins at about 1075°C. As for yttrium, there is probably an incongruent melting of $\text{Gd}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ into $\text{Gd}_2\text{BaCuO}_5$ and a liquid.

The DTA curve of $\text{Gd}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ in nitrogen atmosphere is given in Figure 4. As for $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$, there is a displacement of the peaks toward low temperatures compared to the thermogram obtained in oxygen atmosphere. In inert atmosphere, the Gd perovskite begins to melt at about 990°C.

The pattern of the thermogravimetric curve (heating) in nitrogen atmosphere for the Gd compound is shown in Figure 5 and is similar to the one obtained with yttrium. There is a sudden loss of weight starting at about 400°C, which is at a temperature slightly lower than for $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$, accompanied with a change of slope at about 560°C. Thus, the transition orthorhombic to tetragonal is also probably present with $\text{Gd}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ as they have a similar crystal structure. However, this transition occurs at lower temperature compared to the Y compound.

The TG curve of $\text{Gd}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ in oxygen atmosphere on heating is shown in Figure 6 and indicates that this compound captures oxygen at a lower temperature (250°C) than the Y compound (325°C). The maximum gain of weight (330°C) is also achieved more rapidly than with $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ with a ΔT of 80°C, but the increase is similar with about 1.3%.

Thus, the energy required to insert oxygen atoms into the crystal structure is smaller for the Gd than for Y compound.



The superconductor made with neodymium has the highest superconducting transition temperature, T_c , compared to Y or Gd [3,15]. Figure 7 shows the DTA curve of $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ in oxygen atmosphere. Clearly, there are less impurities or secondary phases in this compound since there are few peaks in the thermogram. As for the previous perovskites, the endothermic peak at about 815°C is probably caused by the α - β transition of BaCO_3 .

$\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ begins to melt at about 1107°C in oxygen atmosphere which is a higher temperature than for Y or Gd perovskites. In fact, there is nominally linear trend between the ionic radius of the rare earth element and the cell volume [15]. There is also a relation between T_c and the ionic radius, and our result indicates that there is a relation between the ionic radius and the onset melting temperature. For the three rare earth used in this study, an increase in the ionic radius is proportional to an increase of the onset melting temperature. In nitrogen atmosphere, $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ begins to melt at about 1035°C as shown in Figure 7.

The TG curve of $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ in nitrogen atmosphere on heating is similar to the curve obtained with $\text{Gd}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ (Figure 8). The loss of weight starts at about 400°C and there is change of slope at about 550°C. Thus, it is highly probable that the transition involving the orthorhombic structure is also present with the Nd compound. The TG

curve obtained in oxygen atmosphere, illustrated in Figure 9, indicates that the compound captures oxygen at about 330°C with a maximum at about 420°C which correspond to a ΔT of 90°C, but the gain of weight is about 1.7% which higher than for Y or Gd compounds. As for Gd, the energy required to incorporate oxygen is smaller than for Y compound.

CONCLUSION

DTA curves of the studied cuprate perovskites are relatively similar. In oxygen atmosphere, $Y_1Ba_2Cu_3O_{7-x}$, $Gd_1Ba_2Cu_3O_{7-x}$ and $Nd_1Ba_2Cu_3O_{7-x}$ begins respectively to melt at 1030°C, 1075°C and 1107°C. In nitrogen atmosphere, these values are shifted down to 965°C, 990°C and 1035°C respectively. In fact, there is a relation between the ionic radius of the rare earth and the onset melting temperature. The DTA curves indicate the presence of impurities or secondary phases in the perovskites. Based on our result, the behavior of $Y_1Ba_2Cu_3O_{7-x}$, $Gd_1Ba_2Cu_3O_{7-x}$ and $Nd_1Ba_2Cu_3O_{7-x}$ during sintering is different and the Nd compound is the most easily synthetized. At 950°C, under the conditions of this study, the system Nd-Ba-Cu-O is the most favorable to the formation of the 123 superconductor followed by the Y system, and finally by the Gd system.

Thermogravimetric experiments have suggested the presence of a transition orthorhombic to tetragonal (550-600°C) in the three studied compounds. Also, TG curves have shown that $Gd_1Ba_2Cu_3O_{7-x}$ reacts with oxygen at a lower temperature than $Y_1Ba_2Cu_3O_{7-x}$ or $Nd_1Ba_2Cu_3O_{7-x}$. However, the cycle absorption-desorption of oxygen is reversible for the three compounds.

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